

Thermal poling of glass modified by gamma radiation

Olivier Deparis*, Costantino Corbari, Peter G. Kazansky
Optoelectronics Research Centre (ORC), University of Southampton, United Kingdom
Benoît Brichard**, Francis Berghmans, Marc Decréton
SCK•CEN, Belgium

ABSTRACT

Flame-fused type-II silica glass and synthetic type III silica glass were exposed to gamma radiation and then thermally poled. Second-harmonic generation (SHG) is reduced by several orders of magnitude in Suprasil glass for doses higher than 100 kGy and in Herasil glass for doses higher than a few MGy. In Herasil glass, however, SHG is unchanged for doses lower than about one MGy. In the latter case, Maker fringe measurements show that, like in the poled pristine glass, the second-order nonlinearity is located in a thin layer beneath the anodic surface. On the other hand, in the former case, Maker fringe measurements reveal the existence of weak bulk nonlinearity. This unexpected result suggests that dipole orientation takes place in the glass modified by gamma radiation.

Keywords: Thermal Poling, Radiation, Defects, Second-Harmonic Generation, Nonlinear Optics

1. INTRODUCTION

Even-order nonlinear optical interactions are forbidden in glass because of the macroscopic inversion symmetry of the amorphous network. Thermal poling breaks this symmetry and, consequently, creates a permanent effective second-order susceptibility $\chi^{(2)}$ in the glass. Based on poled glass, active planar waveguide or optical fiber devices can be developed for electro-optic switching, wavelength conversion, parametric amplification and oscillation¹. In thermally poled flame-fused silica glass plates, for example, a effective $\chi^{(2)}$ of the order of ≈ 1 pm/V is induced in a thin layer (≈ 10 μ m) beneath the anodic surface of the sample². When the voltage is applied to the heated glass the migration of sodium ions, which are present in the glass as impurities, leads to the formation of a space charge in a thin layer beneath the anodic surface. The space charge field is frozen in the glass during cooling with the voltage applied. The effective $\chi^{(2)}$ is due to the interaction of the frozen-in field E_{DC} and the third-order nonlinear susceptibility of the glass $\chi^{(3)}$, according to $\chi^{(2)} = 3\chi^{(3)}E_{DC}$. In principle, the orientation of electric dipoles, which may be present in the glass in the form of polar bonds, can also take place under the action of the applied electric field. The freezing of oriented dipoles leads to a $\chi^{(2)}$ in the whole bulk of the glass. The frozen-field mechanism accounts well for the magnitude and the symmetry properties of the second-order nonlinearity in thermally poled silica glass³. However, one can not exclude the possibility of dipole orientation under the action of the frozen-in field itself. On the other hand, the coexistence of near-surface nonlinearity and bulk nonlinearity has been reported⁴, indicating that the dipole orientation could take place in the whole bulk.

Exposure to high-energy photons (X-rays, gamma rays) or particles (electrons, neutrons, etc.) is known to dramatically modify the glass structure through the creation of point defects⁵. When the glass is exposed to gamma rays (1 MeV) the radiation-matter interaction begins by the production of energetic Compton electrons, which subsequently produce secondary electrons and electron-hole pairs by ionization. Electrons and holes move in the glass network until they recombine or are trapped at precursor sites such as dangling bonds or wrong bonds, leading to the formation of defects in the latter case. The activation of precursor sites by charge trapping is a reversible process, since the trapped charges can be thermally released. Thermal annealing is not only responsible for the decay of defect populations after irradiation but also for the dependence of defect populations on the dose rate during irradiation. On the other hand, new defects can be created during irradiation by rupture of bonds. Defects can absorb or emit light, mostly in the ultraviolet and the visible, by electronic transitions between their energy levels which are located within the band gap (≈ 9 eV in silica), at the top of the valence band or at the bottom of the conduction band. Defects can be paramagnetic or diamagnetic, electrically neutral or charged.

* old@orc.soton.ac.uk; phone 44 23 8059 3139; fax 44 023 8059 3142; <http://www.orc.soton.ac.uk>; Optoelectronics Research Centre, University of Southampton, Southampton SO17 1BJ, United Kingdom; ** bbrichar@sckcen.be; phone 32 14 332640; fax 32 14 311993; <http://www.sckcen.be>; SCK•CEN, Boeretang 200, B-2400 Mol, Belgium.

Most likely defects have an impact on the thermal poling of glass. The presence of broken bonds and trapped charges may influence the migration of ions in the glass network and, consequently, the creation of the frozen-in electric field. Moreover, some defect structures may exhibit electronic hyperpolarizability, forming dipoles which can be oriented under the action of the applied electric field. In the past, it has been reported⁶ that silica glass exposed to gamma radiation exhibits enhanced second-harmonic generation (SHG) when it is thermally poled. More specifically, the second-order nonlinear susceptibility induced by thermal poling was found to increase with an increase in the gamma-ray dose. To explain this effect, it was speculated that radiation-induced defects produce electric dipoles which are oriented in the direction of the applied electric field during poling and then frozen in the glass when it is cooled to room temperature with the voltage still applied. Although promising, this result has been reported only for synthetic type-III silica glass which was irradiated at doses of 10 kGy and 100 kGy. On the other hand, all the poling parameters being identical, poled type-II silica exhibits higher second-order optical nonlinearity than poled type III silica.

In this paper, we report on thermal poling of glass modified by gamma radiation. Type-II silica glass (Herasil) and type-III silica glass (Suprasil) are exposed to gamma-rays from Cobalt-60 sources at high dose rates (tens of kGy/h) and total doses (from one hundred kGy to a few MGy) and then thermally poled at 280 °C and 4 kV. Radiation-induced defects are investigated through optical absorbance spectral measurements using ultraviolet-visible-infrared spectrometer. Second-harmonic generation (SHG) in the poled glass is investigated through Maker fringe measurements using a mode-locked and Q-switched Nd:YAG laser (1064 nm). Exposure of the glass to gamma radiation before poling leads to a drastic reduction of SHG in Suprasil glass for doses higher than hundred kGy and in Herasil glass for doses higher than a few MGy. In both cases, Maker fringe measurements reveal the existence of weak bulk nonlinearity, instead of near-surface nonlinearity.

2. SAMPLES UNDER TEST, IRRADIATION AND THERMAL POLING CONDITIONS

Samples under test are Herasil 1 and Suprasil 1 glass plates. Herasil 1 is a flame-fused (type-II) silica glass with alkali metal impurities (1 ppm Na) and 250 ppm OH content. Suprasil 1 is a synthetic (type-III) silica glass with low impurity level and 1000 ppm OH content. Dimensions of Herasil samples and Suprasil samples are 25×25×0.53 mm and 25×25×1 mm, respectively. The samples are exposed to gamma rays from Co⁶⁰ elements in the underwater irradiation facility BRIGITTE of SCK•CEN, Belgium. The irradiation is carried on at constant temperature (55 °C). The samples are placed on stainless steel holders which are mounted perpendicularly to the axis of the container. The holder position is selected according to the desired dose rate. Three Herasil samples (H1-H3) and three Suprasil samples (S1-S3) are exposed at a dose rate of 8.16 kGy/h. One Suprasil sample (S4) is exposed to a slightly lower dose rate of 6.10 kGy/h. One sample of each pristine glass is used as a reference (Href1 and Sref1). The total doses range from one hundred kGy to a few MGy (Table 1). Thermal poling consists in heating the glass sample at an elevated temperature, applying a high voltage to the sample for a certain time and then cooling it to room temperature with the voltage still applied. Both irradiated samples and non-irradiated (reference) samples are thermally poled in typical conditions: i.e. 280 °C, 4 kV, 30 min, air atmosphere.

Table 1: Samples under test, dose rates and total doses (for SiO₂ material). H: Herasil silica glass, S: Suprasil silica glass.

Samples	Dose rate (kGy/h)	Dose (kGy)
H1, S1	8.16	6386
H2, S2	8.16	1319
H3, S3	8.16	735
S4	6.10	107

3. EXPERIMENTAL RESULTS

3.1 OPTICAL ABSORBANCE IN THE IRRADIATED GLASS

The optical absorbance spectra of the irradiated samples were measured 14 days after irradiation. After such a time following the irradiation, only long-lived radiation-induced defects are present in the glass. Exposure to ionizing radiation has significantly modified the glass structure in both types of silica, as it is attested by the presence of strong radiation-induced absorption bands, which are located mainly in the ultraviolet (Fig. 1 & Fig. 2).

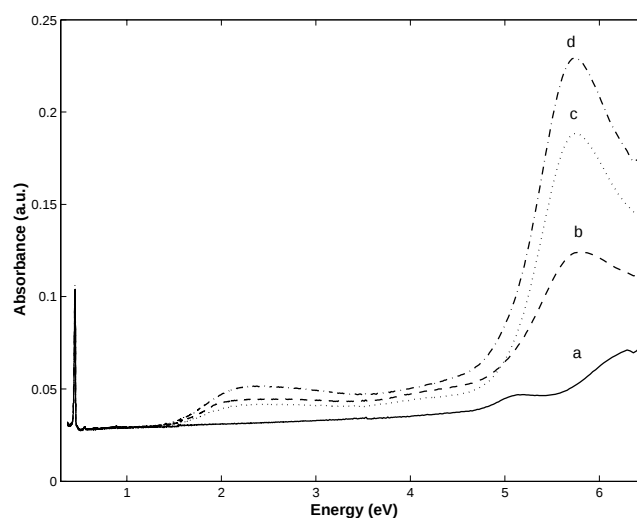


Fig. 1: Optical absorbance spectra in Herasil glass; pristine glass (a); gamma-irradiated glass: 0.7 MGy (b), 1.3 MGy (c), 6.4 MGy (d); dose rate: 8.16 kGy/h (b-d).

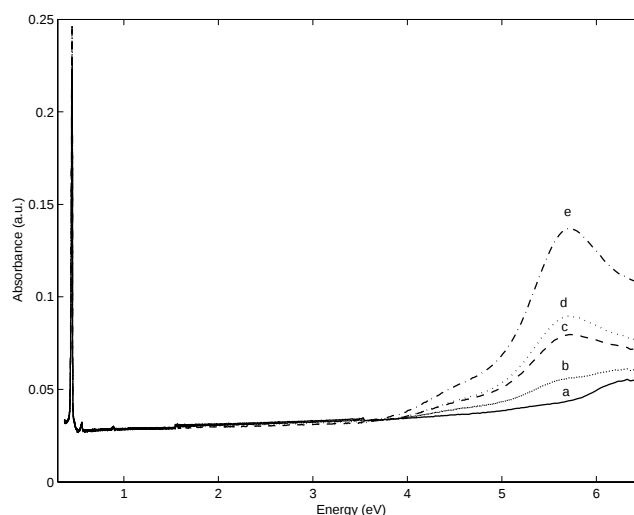


Fig. 2: Optical absorbance spectra in Suprasil glass; pristine glass (a); gamma-irradiated glass: 0.1 MGy (b), 0.7 MGy (c), 1.3 MGy (d), 6.4 MGy (e); dose rate: 6.10 kGy/h (b), 8.16 kGy/h (c-e).

The absorption band around 5.7 eV (215 nm), which is the dominant one in both irradiated Herasil and Suprasil samples, is associated with the E' defect centers⁵, i.e. an unpaired spin in a dangling tetrahedral orbital of an under-coordinated silicon atom ($\equiv\text{Si}\cdot$). In the irradiated Herasil samples, the broad absorption in the visible range (1.8-3.1 eV) is probably due to the superposition of various bands⁷: around 2.0 eV associated with non-bridging oxygen hole centers ($\equiv\text{Si}-\text{O}\cdot$) and peroxy-radical centers ($\equiv\text{Si}-\text{O}-\text{O}\cdot$) and a band around 2.4 eV associated with Al impurity-related defects⁸. In the irradiated Suprasil samples, the absorption tail between 4 eV and 5 eV comes from bands associated with oxygen-deficient centers ($\equiv\text{Si}-\text{Si}\equiv$)⁵. Finally, the infrared absorption peak at 0.453 eV (2.7 μm), observed in both types of silica, is associated with the stretching vibration mode of hydroxyl groups in the silica network ($\equiv\text{Si}-\text{OH}$). The intensity of this peak is higher in Suprasil than in Herasil due to the higher OH content in the former type of silica.

Table 2: Central energy and wavelength of the E' band and of the OH peak.

Samples	E' band		OH peak	
	Energy (eV)	Wavelength (nm)	Energy (eV)	Wavelength (μm)
H1-H3	5.7524	214.5	0.4534	2.722
S1-S4	5.7211	215.7	0.4533	2.722

3.2 SECOND-HARMONIC GENERATION IN THE POLED IRRADIATED GLASS

3.2.1 SHG experimental set-up

Second-harmonic generation is investigated in the poled irradiated glass samples using a Q-switched and mode locked Nd:YAG laser operating at the wavelength of 1.064 μm (Fig. 3). The sample is placed on a rotation stage in such a way that the nonlinear layer is perpendicular to the plane of incidence and the p-polarized fundamental light beam (1.064 μm) impinges on the sample anodic surface at an angle (Fig. 3, inset). Second-harmonic light (0.532 μm) is generated while the fundamental light propagates inside the nonlinear layer and is detected at the output of the sample. For Maker fringe measurements, the intensity of the transmitted SH light is measured as a function of the incident angle θ .

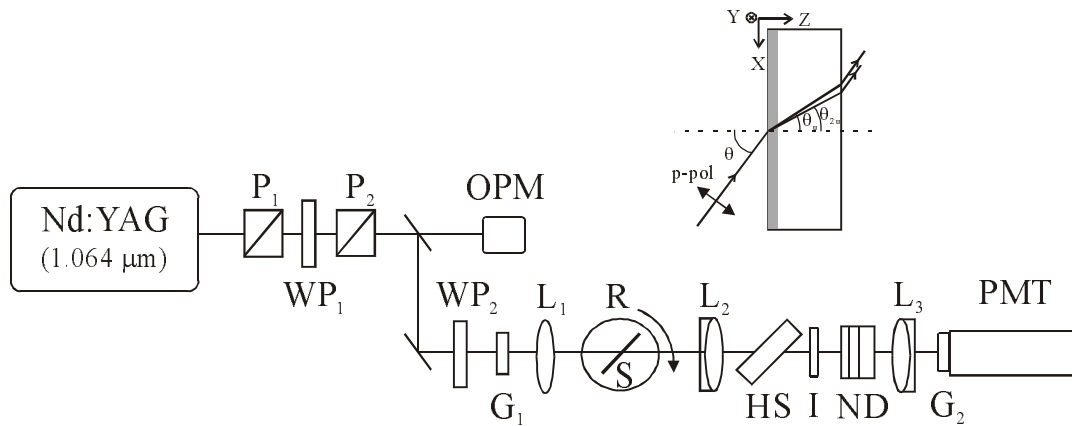


Fig. 3: SHG experimental set-up. Nd:YAG: Q-switched and mode-locked Nd: YAG laser; S: sample; R: rotation stage; P: polarizer; WP: half-wave plate; L: lens; G₁: green (0.532 μm) blocking filter; G₂: green narrow pass-band filter; I: infrared (1.064 μm) blocking filter; HS: harmonic separator; ND: neutral density filters; OPM: optical power meter; PMT: photomultiplier tube. Inset: pump beam polarization and sample geometry (rotation around Y axis).

The measured Maker fringe curves are fitted to the theoretical dependence of the transmitted SH power $P_{2\omega}$ on the incident angle θ :

$$P_{2\omega} = K \frac{aT}{n_{2\omega}n_{\omega}^2} (d_{\text{eff}})^2 \left(\frac{w}{\cos \theta_{2\omega}} \right)^2 \text{sinc}^2(\varphi) \quad (1)$$

where K is a constant, n_{ω} and $n_{2\omega}$ are the refractive indexes of the glass at fundamental and SH wavelength respectively, $a(\theta)$ is a beam correction factor, $T(\theta) = T_{2\omega}(T_{\omega})^2$ is an overall Fresnel transmission factor, $d_{\text{eff}}(\theta)$ is the effective second-order nonlinear coefficient, w is the thickness of the nonlinear layer, $\theta_{2\omega}(\theta)$ is the angle at which the SH light propagates inside the glass, $\varphi(\theta)$ is a phase shift. The angle dependence of the SH power is mainly determined by $d_{\text{eff}}(\theta)$ and $\varphi(\theta)$, whose expressions are respectively:

$$d_{eff} = d_{33} \left(\frac{1}{3} \cos \theta_{2\omega} \sin(2\theta_{2\omega}) + \sin \theta_{2\omega} \left(\frac{1}{3} \cos^2 \theta_{\omega} + \sin^2 \theta_{\omega} \right) \right) \quad (2)$$

and

$$\varphi(\theta) = \frac{\Delta k}{2} \frac{w}{\cos \theta_{2\omega}} \quad (3)$$

In eq. (2), $d_{33} = \frac{1}{2} \chi_{zzz}^{(2)}$ and $\theta_{\omega}(\theta)$ is the angle at which the fundamental light propagates inside the glass. In eq. (3), $\Delta k = 4\pi/\lambda \times [n_{2\omega} - n_{\omega} \cos(\theta_{\omega} - \theta_{2\omega})]$ is the wave vector mismatch projected along the propagation direction of the SH light. In silica $\theta_{\omega} \approx \theta_{2\omega}$, implying that $\Delta k = \pi/l_c$ where $l_c = \lambda/4 \times (n_{2\omega} - n_{\omega})$ is the coherence length of the nonlinear interaction ($\approx 24 \mu\text{m}$ in silica). The sinc^2 factor in eq. (1) is responsible for a fringe pattern in the dependence of the SH power on the incident angle, provided that the nonlinear thickness is larger than the coherence length. Usually fringe pattern is not observed in thermally poled silica glass since $w < l_c$. Instead, the SH power increases as the incident angle increases, reaches a maximum around 60° , and then decreases sharply because of Fresnel losses. The poled reference glass samples exhibits this typical behavior (Fig. 4), indicating that the nonlinear thickness is lower than the coherence length. SHG in the poled Herasil reference sample is about 7.3 times higher than in the poled Suprasil reference sample.

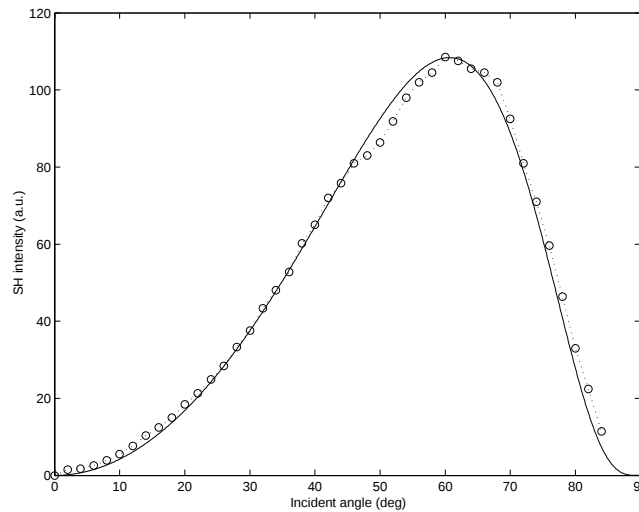


Fig. 4: Maker fringe measurement (circles) on Herasil (non-irradiated) glass sample and best fit (line) to the theoretical curve of eq. (1) using $w = 5 \mu\text{m}$.

3.2.2 Measurements at fixed incident angle

For a comparison between the poled samples, we define a normalized SHG as:

$$SHG = \frac{P_{2\omega}}{F \times P_{2\omega,ref}} \quad (4)$$

where $P_{2\omega}$ and $P_{2\omega,ref}$ are the transmitted SH powers measured for the poled irradiated sample and the poled reference sample, respectively, and F is a scale factor whose value is determined by the neutral density optical filters used in the

measurements. SHG measurements are performed at 60 degree incident angle of the pump beam, for which thermally poled silica glass usually exhibits maximum SHG. The results are summarized in Table 3. In poled Herasil glass, SHG is almost unchanged in the two samples irradiated at 0.7 MGy and 1.3 MGy while it is reduced by four orders of magnitude in a sample irradiated at 6.4 MGy. This result suggests that gamma radiations have no impact on subsequent poling of the glass below some critical dose level while they affect dramatically the poling above that level. The critical dose level below which thermal poling is not altered by gamma radiation pre-treatment is remarkably high in the case of type II silica glass. In poled Suprasil glass, SHG is reduced by four orders of magnitude in all the irradiated samples. In the past, enhancement of SHG was reported⁶ in the same type of silica glass (type III) having received a gamma ray dose of 100 kGy (dose rate not specified). At the same dose level (S4), a drastic reduction of SHG is observed in poled Suprasil glass, in contradiction with the previous result. The residual SHG depends on the total dose and the dose rate: surprisingly, it is slightly higher for higher doses (Table 3).

Table 3: Results of SHG tests at an incident angle of 60°; SHG in poled irradiated samples H1-H3 (S1-S4) is normalized to SHG in poled reference sample Href1 (Sref1). F is an intensity scale factor.

Sample	Dose (kGy)	Scale factor F	Norm. SHG
H1	6386	2000	$1.52 \cdot 10^{-4}$
H2	1319	1	1.00
H3	735	1	0.99
S1	6386	2000	$8.13 \cdot 10^{-4}$
S2	1319	2000	$6.03 \cdot 10^{-4}$
S3	735	2000	$3.40 \cdot 10^{-4}$
S4	107	2000	$3.68 \cdot 10^{-4}$

3.2.3 Maker fringe measurements

In the Herasil samples which were exposed to doses lower than 1.3 MGy before poling, the dependence of the SH intensity on the incident angle is the same as in the poled reference sample (Fig. 5). The measured curve is well fitted using eq. (1), assuming the nonlinearity is located in a thin layer underneath the anodic surface.

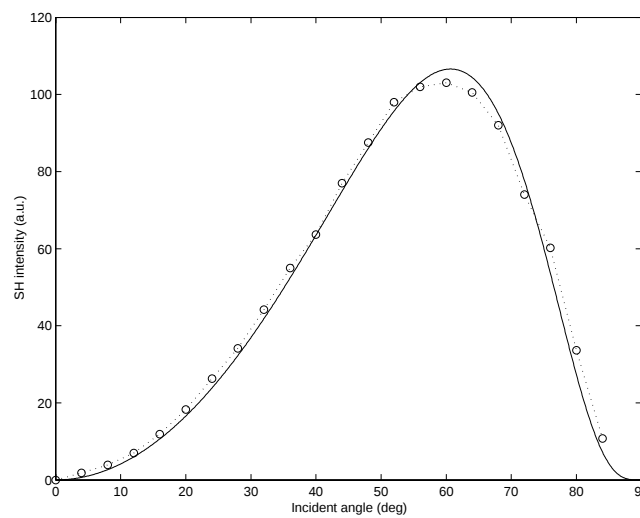


Fig. 5: Maker fringe measurement (circles) on poled irradiated Herasil glass (H2) and best fit (line) to the theoretical curve of eq. (1) using $w = 5 \mu\text{m}$.

In the Herasil sample which was exposed to a dose of 6.4 MGy, the dependence of the SH intensity on the incident angle exhibits fringes with four maxima between 0 and 80° (Fig. 6). The value of the nonlinear thickness leading to the best fit of the measured curve is in good agreement with the nominal thickness of the sample (530 μm). This

unexpected result is a strong indication that the nonlinearity, although very weak, is distributed in the whole bulk rather than in a thin layer underneath the anode. We speculate that the weak nonlinearity in the poled irradiated glass originates from dipole orientation in the bulk. In the Suprasil samples, the dependence of the SH intensity on the incident angle exhibits fringes with eight maxima between 0 and 80 degree (Fig. 7). The nonlinear thickness leading to the best fit is in good agreement with the nominal thickness of the sample (1000 μm), again suggesting the existence of a weak bulk nonlinearity.

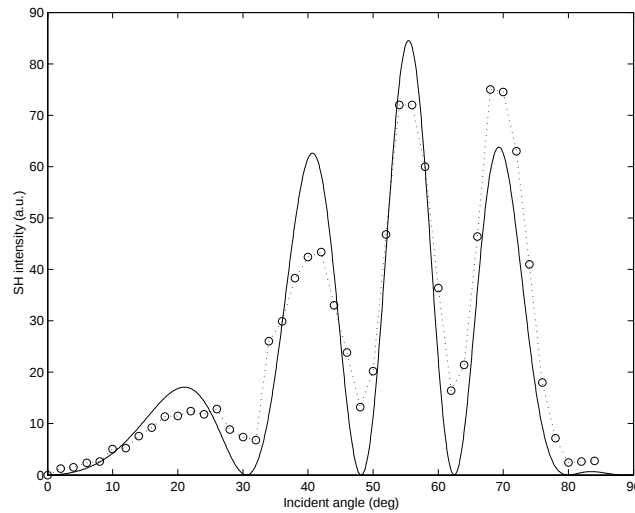


Fig. 6: Maker fringe measurement (circles) on poled irradiated Herasil glass (H1) and best fit (line) to the theoretical curve of eq. (1) using to $w = 494 \mu\text{m}$.

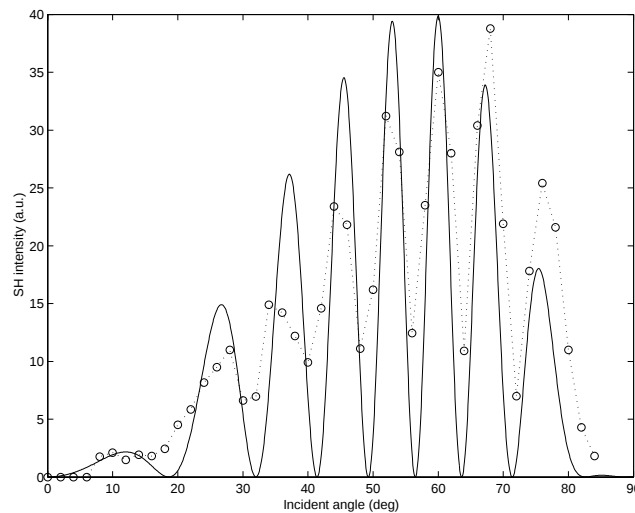


Fig. 7: Maker fringe measurement (circles) on poled irradiated Suprasil glass (S1) and best fit (line) to the theoretical curve of eq. (1) using to $w = 982 \mu\text{m}$.

4. CONCLUSION

Commercial silica glass plates (Herasil and Suprasil) were exposed to gamma radiation at kGy/h dose rate and then thermally poled at 280 °C and 4 kV. SHG is reduced by four orders of magnitude in Suprasil glass for doses higher than 100 kGy and in Herasil glass for doses higher than a few MGy. In Herasil glass, however, SHG is

unchanged for doses lower than about one MGy. In the latter case, Maker fringe measurements show that, like in the poled pristine glass, the second-order nonlinearity is located in a thin layer beneath the anodic surface. On the other hand, in the former case, Maker fringe measurements reveal the existence of weak bulk nonlinearity. This unexpected result suggests that dipole orientation takes place in the glass modified by gamma radiation.

On the basis of the present results, it is clear that radiation-induced defects have a strong impact on the thermal poling of silica glass. To some extent, the modifications induced in the glass structure by gamma radiation are reversible, e.g. through thermal annealing of defects. An appropriate treatment of the poled irradiated glass might be able to restore partially SHG to its level in the poled pristine glass. Therefore, if such a treatment could be applied selectively to the glass, it would offer a new method for fabrication of second-order nonlinear susceptibility grating.

ACKNOWLEDGMENT

This research has been partially supported by the EEC: GLAMOROUS project.

REFERENCES

1. P. G. Kazansky, P. St. J. Russell, and H. Takebe, "Glass fiber poling and applications," *J. of Lightwave Techn.* **15**, pp. 1484-1493, 1997.
2. R. A. Myers, N. Mukherjee, and S. R. J. Brueck, "Large second-order nonlinearity in poled fused silica," *Opt. Lett.* **16**, pp. 1732-1734, 1991.
3. P. G. Kazansky, and P. St. J. Russell, "Thermally poled glass: frozen-in electric field or oriented dipoles?," *Opt. Comm.* **110**, pp. 611-614, 1994.
4. L. J. Henry, A. D. DeVilbiss, and T. E. Tsai, "Effect of preannealing on the level of second-harmonic generation and defect sites achieved in poled low-water fused silica," *J. of Opt. Soc. of Am. B* **12**, pp. 2037-2045, 1995.
5. D. L. Griscom, "Optical properties and structure of defects in silica glass," *J. of Ceram. Soc. Of Japan.* **99**, pp. 923-942, 1991.
6. K. Tanaka, K. Kashima, K. Hirao, N. Soga, S. Yamagata, A. Mito, and H. Nasu, "Effect of gamma-irradiation on optical second harmonic intensity of electrically poled silica glass," *Jpn. J. Appl. Phys.* **34**, pp. 173-174, 1995.
7. D. L. Griscom, and M. Mizuguchi, "Determination of the visible range optical absorption spectrum of peroxy radicals in gamma-irradiated fused silica", *J. of Non-Cryst. Sol.* **239**, pp. 66-77, 1998.
8. C. D. Marshall, J. A. Speth, S. A. Payne, "Induced optical absorption in gamma, neutron and ultraviolet irradiated fused quartz and silica," *J. of Non-Cryst. Sol.* **212**, pp. 59-73, 1997.
9. P. D. Maker, R. W. Terhune, M. Nisenoff, C. M. Savage, "Effects of dispersion and focusing on the production of optical harmonics," *Phys. Rev. Lett.* **8**, pp. 21-22, 1962.